PB-230 827

FWPCA METHOD STUDY 1: MINERAL AND PHYSICAL ANALYSES

Federal Water Pollution Control Administration
Cincinnati, Ohio

June 1969

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An Evaluation of FWPCA Analytical Methods for Surface Waters

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Cincinnati, Ohio 45202

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An Evaluation of FWPCA Analytical Methods for Surface Waters

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Acknowledgements

The authors wish to acknowledge the technical assistance of Mr. Elmo Julian, Supervisory Chemist, AQCL, and Dr. Ralph Harkins and Mr. Jimmie Kingery, Mathematical Statisticians at Kerr Water Research Center in the design and operation of the computerized statistic programs, developed for this study.

Participating Laboratories

Fifty-one analysts in twenty-five laboratories took part in FWPCA Method Study 1. Of these, five were non-FWPCA laboratories. The participating laboratories were:

FWPCA Laboratories

Alaska Water Lab.
College, Alaska

California-Nevada Basins Lab.
Alameda, California

Chesapeake Technical Support Lab.
Annapolis, Maryland

Cincinnati Water Research Lab.
Cincinnati, Ohio

Colorado River-Bonneville Basins Lab.
Salt Lake City, Utah

Hudson-Delaware Basins Office
Edison, New Jersey

Lake Erie Basin Office
Cleveland, Ohio

Lake Huron Basin Office
Gross Ile, Michigan

Lake Michigan Basin Office
Chicago, Illinois

Lower Miss. River Basins Comp. Project
Baton Rouge, Louisiana

Lower Ohio Basin Office
Evansville, Indiana

Missouri Basin Laboratory
Kansas City, Missouri

National Field Investigations Center
Cincinnati, Ohio

National Marine Water Quality Lab.
West Kingston, Rhode Island

New England Basin Office
Needham Heights, Massachusetts

Pacific Northwest Water Lab.
Corvallis, Oregon

R. S. Kerr Water Research Center
(Research) Ada, Oklahoma

R. S. Kerr Water Research Center
(Technical Programs) Ada, Oklahoma

Southeast Water Laboratory
Athens, Georgia

Upper Ohio Basin Office
Wheeling, West Virginia

Other

Bowser-Morner Testing Labs., Inc.
Dayton, Ohio

Indiana State Board of Health
Indianapolis, Indiana

U.S. Geological Survey
Austin, Texas

U.S. Geological Survey
Denver, Colorado

U.S. Geological Survey
Lincoln, Nebraska

FWPCA METHOD STUDY 1, MINERAL AND PHYSICAL ANALYSES

An Evaluation of FWPCA Analytical Methods for Surface Waters

Summary

Pairs of synthetic water samples were prepared in three ranges of concentration for pH, specific conductance, total dissolved solids total hardness, sodium, potassium, total acidity/alkalinity, chloride and sulfate for analysis by *FWPCA Official Interim Methods for Chemical Analysis of Surface Waters*[1]. Fifty-one analysts from twenty laboratories in FWPCA and 5 non-FWPCA laboratories cooperated in this study. A statistical summary of the results on page 2 indicates the precision and accuracy values obtainable in routine work. For detailed statistics see Figures 1-9.

Statistical Summary

Mineral and Physical Parameters

	Range of Concentration	Accuracy as % Relative Error	Precision as Standard Deviation
pH	3.5-8.0 pH units	0.00% to +1.01%	0.10-0.20 pH units
Specific Conductance	100-1700 umhos/cm	-5.36% to -0.76%	7.55-119 µmhos/cm
TDS	60-1000 mg/l	+1.71% to +15.8%	15.1-70.9 mg/l
Total Hardness	31-444 mg/l $CaCO_3$	-3.35% to -0.19%	2.52-9.65 mg/l $CaCO_3$
Sodium	4.1-155 mg/l	-0.11% to +2.94%	0.14-3.97 mg/l
Potassium	1.4-20.0 mg/l	+4.76% to +8.66%	0.17-1.58 mg/l
Alkalinity	8.0-119 mg/l $CaCO_3$	-8.19% to +22.2%	1.14-5.28 mg/l $CaCO_3$
Chloride	17-398 mg/l	-1.19% to +3.50%	1.32-11.8 mg/l
Sulfate	8.6-199 mg/l	-8.26% to +0.04%	1.78-11.8 mg/l

FWPCA METHOD STUDY 1, MINERAL AND PHYSICAL ANALYSES
An Evaluation of FWPCA Analytical Methods for Surface Waters

Introduction

The Federal Water Pollution Control Administration gathers water quality data to determine compliance with water quality standards, to provide information for planning of water resources development, to determine the effectiveness of pollution abatement procedures, and to assist in research activities. In a large measure, the success of the pollution control program rests upon the reliability of the information provided by the data collection activities.

To insure the reliability of physical, chemical, and biological data, the Division of Water Quality Research has established the Analytical Quality Control Laboratory, at 1014 Broadway, Cincinnati, Ohio. The AQC program, conducted by this laboratory, is designed to assure the validity, and, where necessary, the legal defensibility of all water quality information collected by FWPCA.

The Methods and Performance Evaluation (M&PE) Activity of the Laboratory is responsible for studies for the evaluation of analytical procedures selected for use in FWPCA laboratories. The study reported herein is devoted to analyses for the mineral and physical parameters of water quality and was designed to measure the accuracy and precision of the selected FWPCA analytical methods in the cooperating FWPCA laboratories. The evaluation of results also permits a judgment of the relative capabilities of these laboratories to perform these analyses.

Finally, since this was the first full-scale study conducted by the M&PE Activity, it is a test of the study design, the statistical treatment, and the computer programs used.

Description of the Test

Selection of an Appropriate Test Design

The test designs generally used in interlaboratory studies were reviewed in detail. Youden's non-replicate x, y sample technique[2] was selected as the best measure of methods, laboratories, and analysts. Basically, two similar but different samples were analyzed once by each analyst for each range of concentration. This was considered preferable since it is the way that samples are analyzed normally and it reduces the chance for repetitive analyses or averages to mask the variability in the method.

However, the conclusions possible with the technique were not completely satisfactory. A data treatment was proposed that modified Youden's test design and measured the precision and accuracy of each method and the amount of systematic error due to laboratory bias.

A series of computerized analyses were developed on the IBM 1130 computer for manipulation of test data: A data display program coded EXCOL, a T test program for rejection of outliers coded T-Test, (see Table 2) and a range variance, standard deviation and mean program coded COLV (see Figures 1-9). A glossary of statistical terms used in this study is provided in Appendix A.

Preparation of Samples and Reporting of Results

The six samples for FWPCA Method Study 1 were prepared for analysis of the mineral and physical parameters: pH, total alkalinity or total acidity, specific conductance, total dissolved solids, hardness, sodium, potassium, chloride, and sulfate. Each sample was prepared by appropriate dilution in high-purity distilled water of a series of stock solutions containing known amounts of analytical reagent grade chemicals. After dilution to a final volume of 100 liters, each sample was mixed vigorously for a period of 18 hours. Then one quart portions were withdrawn into plastic bottles (Cubitainers). No preservatives were added.

The set of six samples actually comprised three pairs, with each member of a pair being closely related in concentration to the other. Samples 1 and 2, 3 and 4, and 5 and 6 are paired in this manner. This design is such that the maximum information can be gained without resorting to duplicate analyses.

The stability of the samples was checked by repeated analyses over a period of about two months, first through a pilot stage, and then the full-scale 100 liter batch. Repetitive analyses performed by the Methods and Performance Evaluation laboratory and by an independent referee laboratory confirmed the concentrations of the various ions. Values which vary in relation to the constitution of the sample (pH, specific conductance, and total dissolved solids) were established by laboratory analysis. The chemical composition of the samples is shown in Table 1.

TABLE 1

True Values*, FWPCA Method Study 1

	Sample					
Parameter	1	2	3	4	5	6
pH	7.1	7.2	3.5	3.5	8.0	8.0
Sp Conductance (µmhos at 25°C)	106	100	848	808	1710	1640
Total Dissolved Solids (mg/l)	62	60	442	416	1000	958
Total Hardness (as mg/l $CaCO_3$)	33	31	194	182	444	417
Sodium (mg/l)	4.1	3.8	55	52	155	145
Potassium (mg/l)	1.5	1.4	8.0	7.5	20	19
Total Acidity (as mg/l $CaCO_3$)			21	20		
Total Alkalinity (as mg/l $CaCO_3$)	9	8			119	113
Chloride (mg/l)	18	17	97	91	398	382
Sulfate (mg/l)	9.2	8.6	199	188	122	110

*See Glossary of Terms

The samples were shipped to participating laboratories on September 23, 1968. Detailed instructions for analyses and reporting of results were provided at that time. It was stipulated that only the *FWPCA Official Interim Methods for Chemical Analysis of Surface Waters*[1] were to be used.

To maintain objectivity in data handling and laboratory evaluation, a three digit code number was assigned permanently to each laboratory. Since many laboratories received multiple sets of samples and submitted separate results for each analyst, a temporary letter code was assigned to the analyst. These codes are used throughout this report.

Treatment of Data

Paired-Sample Charts

To effectively describe the values obtained for each parameter a series of two-sample charts (Figures 1-9) were prepared, as suggested by Youden[2]. All results were plotted by parameter without rejection of values. Two results for each set of similar samples (1 and 2, 3 and 4 or 5 and 6) form the coordinates on the x and y axes that determined a single point for each analyst. The distribution of points (analysts) characterizes the method.

If random errors were responsible for the spread of results around the true values, then the data from the sample pair would be equally distributed among the four quadrants (++) (-+) (--) (+-). However, the predominant influence on results is systematic error. The distribution of values is not random but on a 45° slope line in the (--) and (++) quadrants, since a laboratory getting a high or low value on one sample also obtained a high or low value on the similar sample. This distribution of values on a 45° slope forms an elliptical pattern. Data points far removed from the elliptical cluster indicate large systematic error for one analyst compared to the other analysts. As random error decreases, data points move even closer to the 45° slope. Extreme values or outliers suggest a procedure or instrument out of control. General scatter indicates poor precision. When all data are spread far out along the 45° line, a large systematic error is indicated for the method as in Figure 9 for Sulfate. When precision is satisfactory but a significant bias occurs the data grouping is low (--) as in Figure 2 for Specific Conductance or high (++) as in Figure 6 for Potassium.

Rejection of Outliers

To display the precision and accuracy of each method, it was necessary to remove those extreme values probably caused by gross instrumental, chemical or human error. These extreme values were rejected by applying the two-tail T-Test to all values at a 99% probability level; that is, with 99% assurance that the data rejected were false and should be rejected. This summary of data rejections

by laboratory and analyst is given in Table 2. In general, poorer precision from greater spreading of data around the true value results in the rejection of fewer outliers. This is because a precision term serves as the denominator in the T-Test and as the precision decreases (number value increases) the calculated T value grows smaller and there are fewer extreme values rejected as outliers. An example of this is the Total Dissolved Solids test. Contrariwise, with better accuracy and precision, the T-Test is more powerful and more outliers are rejected. An example is the total hardness test. However, those data rejected in either case are true outliers and procedures should be carefully reviewed for the causes of inaccuracy.

TABLE 2

Rejection of Outliers by T-Test

Laboratory	Analyst	Parameters								
		pH	Spec. Cond.	TDS	Total Hard.	Sodium	Potass.	Alk-Acid	Chloride	Sulfate
101	A				X		-			
102	A				X	X	-			
103	A									X
103	B						X			
104	A	X	-	-	-	X	X	-	-	-
106	A									
106	B									
107	A									
109	A	X		X		-	-			-
109	B	X		X		-	-			-
109	C	X		X		-	-			-
110	A					-	-		X	-
110	B					-	-			-
110	C					-	-		X	-
110	D					-	-			
110	E				X	-	-			
111	A					-	-			X
11	B				X	-	-			X
112	A									
112	B									
113	A							X		
113	B							X		X
11	A				X	-	-			
114	B					-	-			
114	C		X			-	-			
115	A		X			-	-			
115	B		X			-	-			
115	C		X				X			
116	A									
116	B									
116	C									
116	D									
117	A									X
120	A				X	-	-	X		
120	B				X	-	-			X
121	A					-	-			
121	B				X	-	-			
121	C				X	-	-			
122	A	X				-	-			
123	A					X				
123	B					X	X			
123						X	X			X
125	A				X	-	-	X	-	

X = Outliers
- = Not run

Method and Instrument Surveys

It was desirable to review the options offered in each method and to determine how these might affect the data produced. Further, the choice of instrumentation might influence the results. To evaluate these factors, information was requested from all laboratories taking part in this study. The information was used in the following ways:

1. Any data determined as resulting from a "non-FWPCA method" was deleted before the method evaluation was completed.

2. The alternate steps allowed in each method were noted and a correlation was attempted between the choice of alternates and precision and accuracy obtained by the analyst.

3. A tabulation was made of the make and model of the analytical instruments used. This information is useful for general background and also permitted an attempt at correlation between data quality and specific equipment used.

Conclusions

The Surveys did point out certain procedural alternatives which seem to affect the data produced. These are discussed separately for each parameter.

In general, the evaluation of the data for all laboratories suggest that there is no evidence for correlation of instrumentation with goodness of results. Rather the precision and accuracy obtained seem dependent on the laboratory and on the skill of the analyst.

Although there has been no effort to standardize on specific brand or model instruments, the Instrument Survey compiled in Appendix B shows that the Industrial Instruments Model RC16B2 Specific Conductance Meter and the PE 303 Atomic Absorption Spectrometer are in general use in FWPCA. Although more types of pH meters are in use, one instrument, the Beckman Zeromatic model is in most frequent use.

Results

Statistical Evaluation of Analytical Methods

After extreme data were rejected, the retained data were evaluated and reported in the statistic tables by parameter in Figures 1-9. Since the primary purpose in this initial test was the validation of analytical methods in FWPCA, and outside participation was limited, data from non-FWPCA laboratories was not used in the statistical treatment. It is planned that non-FWPCA data will be included in the evaluation of future studies.

In these tables the complete statistics are developed for each analytical method over the full range of samples. Accuracy is expressed as relative error. Precision is presented as the standard deviation and as the 95% confidence interval. Because all digits were retained during calculations but rounded off to three significant figures for the tables, derivation of one statistic from another within a table may show minor differences from the reported values.

Discussion and Conclusions

pH

The pH test by meter had the best precision and accuracy of the tests used for this study. Its precision is excellent. Of the nine parameters, pH was the only measurement which had a precision value constant for all concentrations (0.1 - 0.2 pH units). This is depicted in Figure 1 by the tight grouping of results around the true values. Likewise, the accuracy was excellent for all 6 samples, ranging from a -0.1% to +1.01% bias.

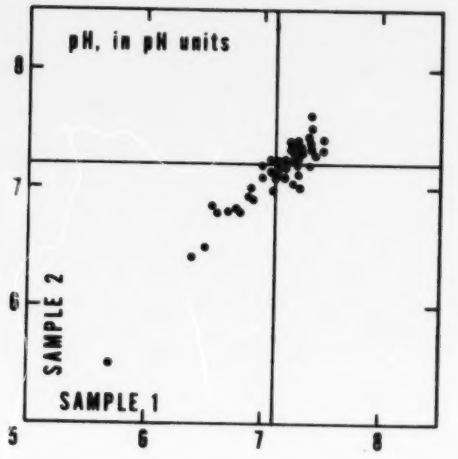
The effect of buffering capacity in the water samples is evident in differences in precision and to a lesser degree, accuracy in the sample sets. The most acidic set of samples, 3 and 4, with a pH of 3.5, shows a tighter grouping of results than the other sample sets. The spread of values at pH 7 and 8 suggests that accurate pH measurements near neutrality are more difficult in routine laboratory operation.

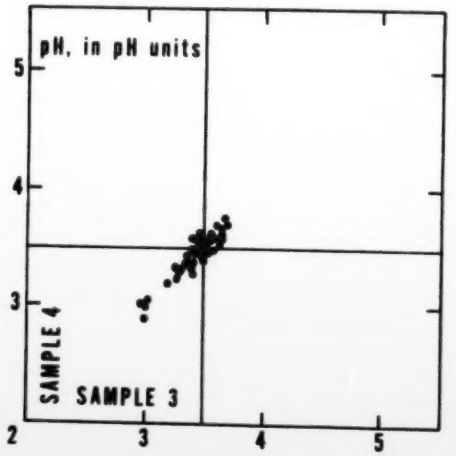
The survey on methods indicates that Standard Methods[4] is the primary reference for most laboratories.

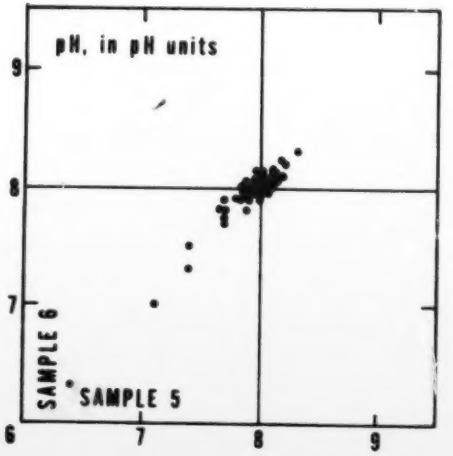
Data from three laboratories were rejected as outliers. All analysts from the laboratory with multiple analysts had values rejected indicating that these outliers were probably related to the laboratory instrument or buffer standard rather than to analysts' technique. This was substantiated in the two sample charts by the spreading out of values along the 45° line suggesting systematic error.

FIGURE 1. TWO-SAMPLE CHARTS & METHOD STATISTICS FOR pH METHOD, FWPCA

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE, pH units	7.1	7.2	3.5	3.5	8.0	8.0
ARITHMETIC MEAN OF REPORTED VALUES, pH units	7.17	7.19	3.48	3.49	7.98	8.01
ACCURACY AS RELATIVE ERROR (% BIAS)	+1.01	-0.03	-0.29	-0.00	-0.12	+0.16
STANDARD DEVIATION, pH units	0.20	0.18	0.10	0.11	0.13	0.12
95% CONFIDENCE INTERVAL pH units	6.78-7.56	6.84-7.54	3.28-3.68	3.27-3.71	7.72-8.24	7.78-8.24







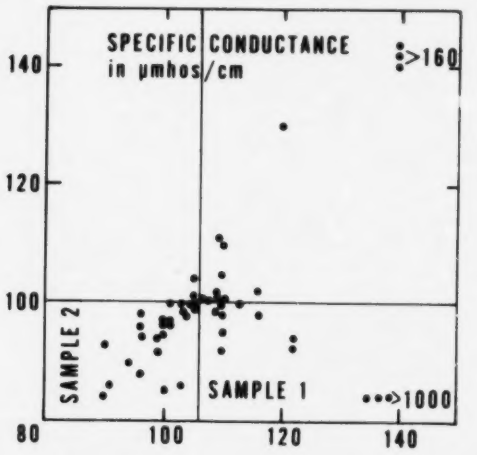
Specific Conductance

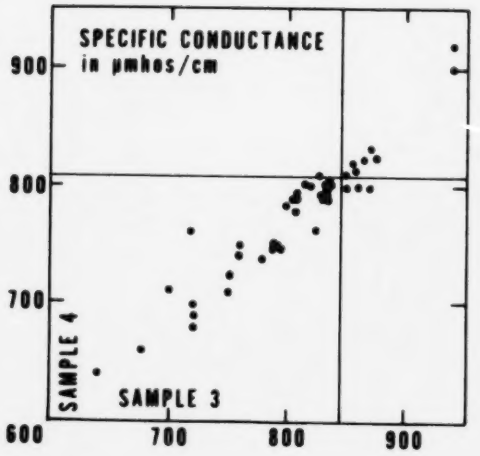
The measurement of conductance by wheatstone bridge was only moderately well performed in this study. The method is reported as reproducible to ± 5% (Standard Methods)[4] and ± 1% (ASTM-referee method)[5] but as seen in Figure 2 the standard deviation for specific conductance in this study ranged from 7.5 µmhos/cm at the 100 µmhos/cm level to 100-115 µmhos/cm at the 1700 µmhos/cm level for a reproducibility of 7.5% and 6.8%, respectively. Accuracy was only fair with a negative bias increasing from a -2% to a -5% as conductance levels increased from 100 to 1700 µmhos/cm. The two-sample charts show a wide scatter along the 45° line indicating definite systematic error in the method. Rather than focussing around the true values, the test data focus at some lower value, indicating poor accuracy and a strong negative bias in this method. Either the method is not as good as reported in the literature (SM or ASTM) or the FWPCA laboratories did not perform as well as could be expected. The general distribution of values for specific conductance was such that the results from only two laboratories were rejected.

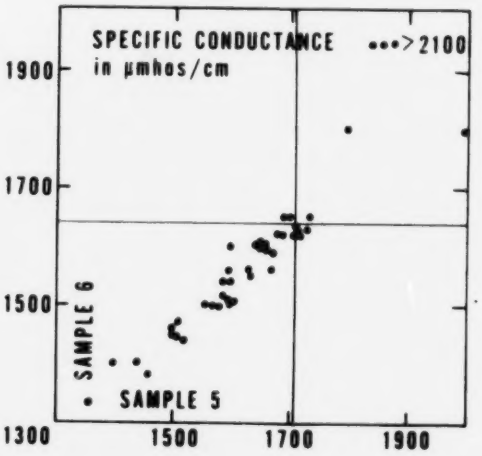
At first, the variety of instrumentation was suspected as a source of deviation. However, it was found that values 1450 to 3300 micromhos were reported on the same sample by laboratories using identical model instruments. The Analytical Method Survey showedthat five participants did not perform the determination at 25°C as specified. However, since data from only one of these five laboratories were rejected as outliers, this temperature variance is not indicated as the primary cause of inaccurate conductance measurements. Rather, closer control over technique and laboratory standards should improve laboratory performance with this method considerably.

FIGURE 2. TWO-SAMPLE CHARTS & METHOD STATISTICS FOR SPECIFIC CONDUCTANCE METHOD, FWPCA

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE, µmhos/cm	106	100	848	808	1710	1640
ARITHMETIC MEAN OF REPORTED VALUES µmhos/cm	105	98	809	779	1620	1550
ACCURACY AS RELATIVE ERROR (% BIAS)	-0.76	-2.02	-4.54	-3.63	-5.08	-5.36
STANDARD DEVIATION, µmhos/cm	8.14	7.55	79.6	66.1	119	106
95% CONFIDENCE INTERVAL µmhos/cm	89.2-121	83.2-113	653-966	650-908	1390-1860	1340-1760







Total Dissolved Solids

The gravimetric determination of dissolved solids showed poor precision, and positive bias at all levels tested. The precision of the total dissolved solids varied inversely with the concentration of solids. There was a surprising 23% relative standard deviation (s.d. as % of mean) at the 60 mg/l levels. This dropped to the 5-10% relative standard deviation level in the samples containing 400-1000 mg solids/liter. Although samples 3 and 4 are a closely matched pair, the standard deviation for sample 4 was twice that for sample 3. No explanation is known for this difference. The general spread of values, was such that only one laboratory was rejected in the test for outliers (See Figure 3).

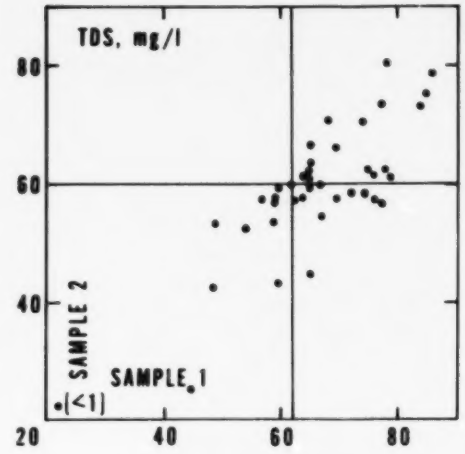
It is believed that the positive bias is due to failure to dry the sample residues to constant weight. According to Standard Methods, 12th ed., Section I, 244: "Constant weight is considered attained when not more than a 0.5-mg weight change occurs between two successive series of operations consisting of heating, cooling in a desiccator, and weighing."[1] Yet on page 243 Standard Methods reports that drying of a residue for one hour at 103°C is usually sufficient to attain constant weight within 0.5 mg. Experience with the reference samples in the M&PE laboratory has shown that drying at 103°C for one hour is not sufficient.

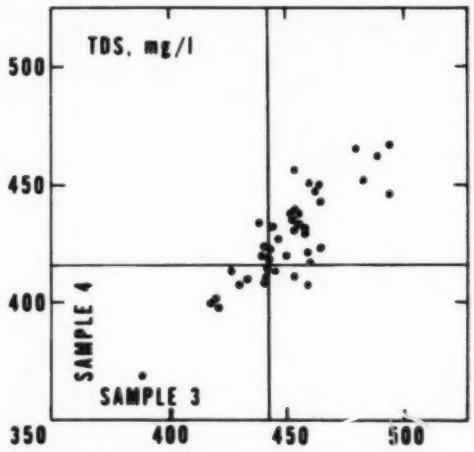
Based on this study there is apparently a need for a clearer and more detailed method write-up to assure greater uniformity between laboratories. Improved precision and accuracy may be obtained by greater emphasis on drying to constant weight. In addition accuracy and precision should be improved by a higher drying temperature.

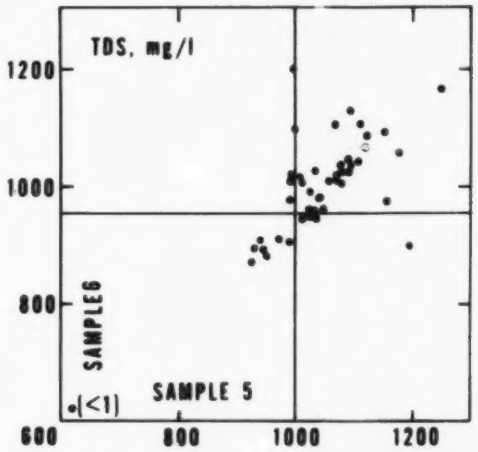
This general feeling was supported in a meeting of the AQC regional coordinators with the AQCL staff in March, 1969 when it was proposed that the second edition of the FWPCA methods manual should direct that total dissolved solids values be obtained only by drying at 180°C.

FIGURE 3. TWO-SAMPLE CHARTS & STATISTICS FOR TOTAL DISSOLVED SOLIDS, FWPCA METHOD

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE, mg/l	62	60	442	416	1000	958
ARITHMETIC MEAN OF REPORTED VALUES, mg/l	71.8	63.5	452	423	1060	1020
ACCURACY AS RELATIVE ERROR (% BIAS)	+15.82	+5.90	+2.21	+1.71	+6.10	+6.69
STANDARD DEVIATION, mg/l	15.1	15.8	24.7	44.4	62.0	70.9
95% CONFIDENCE INTERVAL, mg/l	42.3 - 101	32.6 - 94.5	403 - 500	336 - 510	940 - 1180	883 - 1160







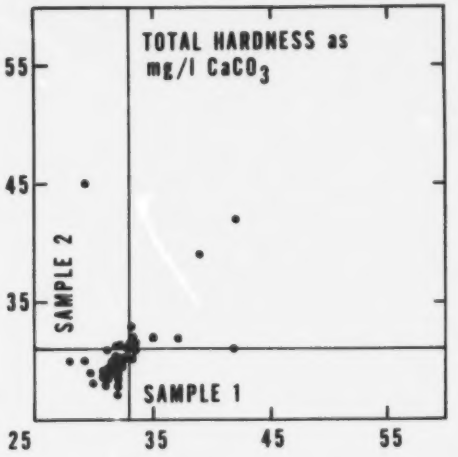
Total Hardness

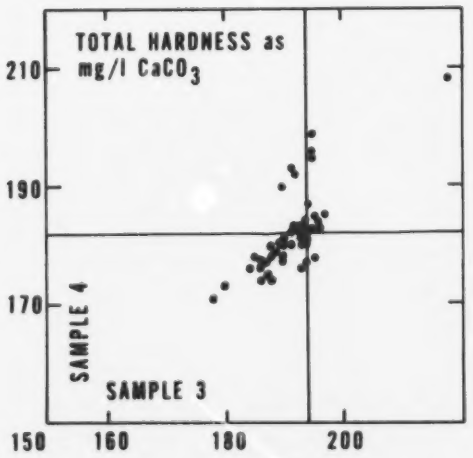
The volumetric test for hardness by EDTA showed excellent results in this study. The tight clustering of hardness values in the two sample charts in Figure 4 reflects the good precision of the test. The charts indicate a good accuracy with a slight negative bias in the method indicated for all samples.

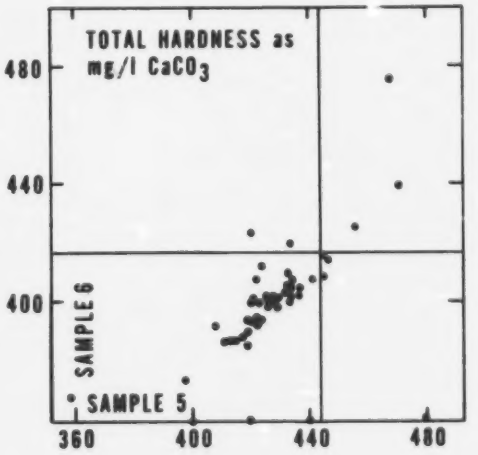
Because of the very good precision of the hardness method, the T-Test for outliers was able to detect outliers extremely well. Of the eight laboratories having outlying values rejected, one laboratory reported high values and seven reported low values. In four of the five laboratories with multiple analyst results, at least one analyst reported acceptable results. This suggests that the analyst factor may be influencing the results for hardness more than the specific procedure, since observation of a colorimetric endpoint is required.

FIGURE 4. TWO-SAMPLE CHARTS & METHOD STATISTICS FOR TOTAL HARDNESS METHOD, FWPCA

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE, mg/l, $CaCO_3$	33	31	194	182	444	417
ARITHMETIC MEAN OF REPORTED VALUES, mg/l $CaCO_3$	32.8	30.7	192	182	430	403
ACCURACY AS RELATIVE ERROR (% BIAS)	-0.73	-0.87	-1.04	-0.19	-3.23	-3.25
STANDARD DEVIATION, mg/l $CaCO_3$	2.52	2.87	2.98	4.87	8.73	9.65
95% CONFIDENCE INTERVAL, mg/l $CaCO_3$	27.8-37.7	25.1-36.4	186-198	172-191	412-447	384-422







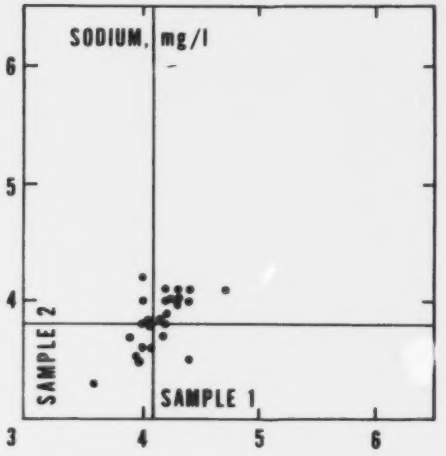
Sodium

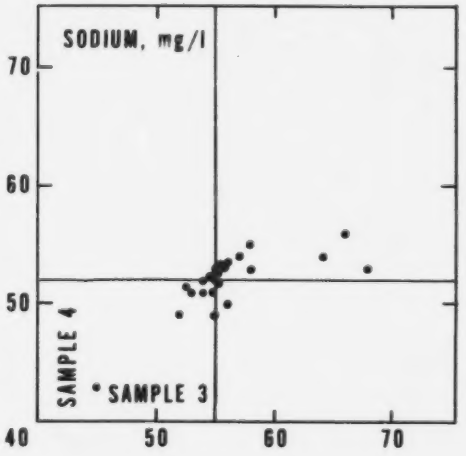
The sodium determination showed excellent precision and accuracy by both atomic absorption and flame photometry. Bias was slight to nonexistent at all levels tested. Atomic absorption was used by 9 of the 12 laboratories. Standard Methods, 12th ed., 277, reports standard deviations of ± 1.3 mg/l and ± 1.8 mg/l by flame photometry for synthetic samples containing 8 mg/l and 19.9 mg/l, respectively.[4] The present study indicates a somewhat better precision, with standard deviation of ± 0.14 and ± 1.99 mg/l at levels of 4.1 and 55 mg/l.

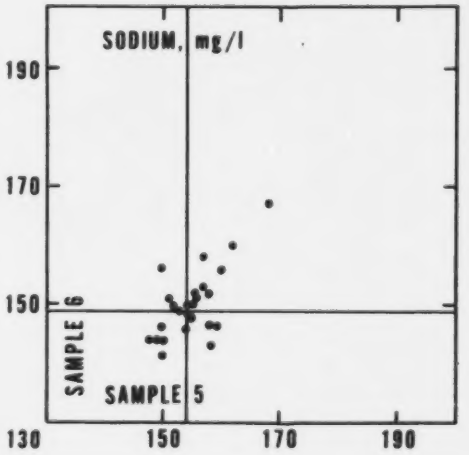
Of 12 laboratories reporting sodium values shown in Figure 5, three laboratories had data rejected because of outliers. All used atomic absorption. Of the laboratories with rejected data, the one with multiple analysts had data rejected for all analysts, suggesting instrument or standards error.

FIGURE 5. TWO-SAMPLE CHARTS & STATISTICS FOR SODIUM, FWPCA METHOD

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE	4.1	3.8	55.0	52.0	155	149
ARITHMETIC MEAN OF REPORTED VALUES, mg/l	4.17	3.91	55.5	52.4	155	149
RELATIVE ERROR (% BIAS)	+1.86	+2.94	+0.90	+0.78	0.00	-0.11
STANDARD DEVIATION	0.14	0.19	1.99	1.93	3.75	3.97
95% CONFIDENCE INTERVAL	3.90-4.44	3.54-4.28	51.6-59.4	48.6-56.2	148-162	141-156







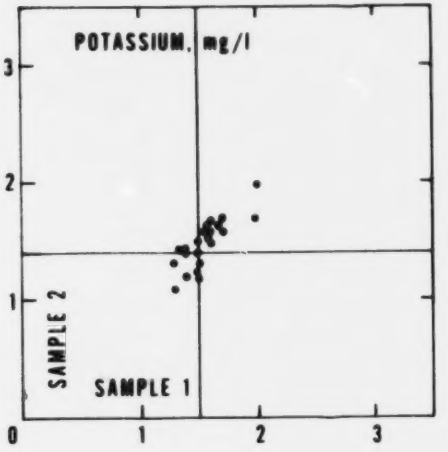
Potassium

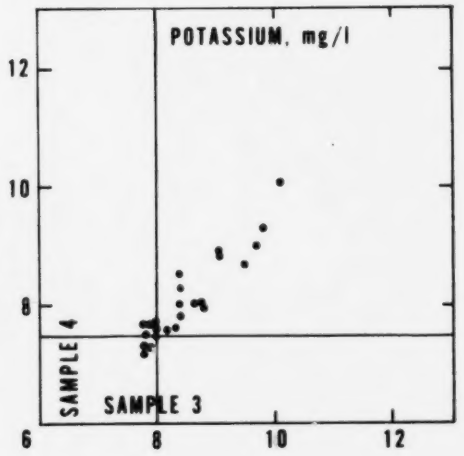
The laboratories performed the potassium analyses with moderate precisions of 0.2 mg/l at a 1.5 mg/l level and 1.35 mg/l at a 20 mg/l level (see Figure 6). A consistent positive bias of 4.8% - 8.7% was evident at the levels tested. All laboratories except two analyzed for potassium by atomic absorption spectroscopy. These two used flame photometry. Fishman[6] reports that sodium exerts a positive interference in the determination of potassium by atomic absorption which may be eliminated by adjustment of samples and standards to contain approximately equal concentrations of sodium (i.e., 200 $\pm$ 50 mg/l). However, many laboratories have found that proper adjustment of the burner height and use of a fuel-rich flame can minimize, if not eliminate, this interference. Four of the ten laboratories had potassium data rejected as outliers. Two of these also had sodium data rejected.

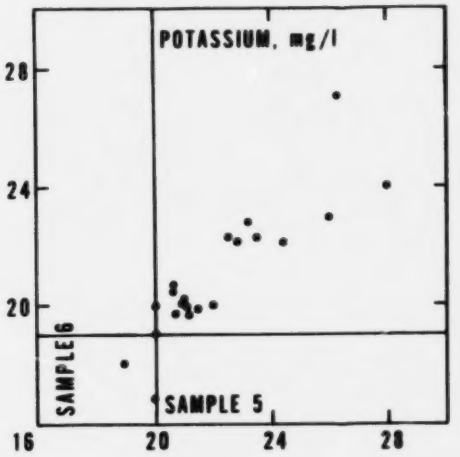
In the Analytical Method Survey, only one laboratory indicated that a correction was made for the above interference. This laboratory reported almost perfect results for samples 1-5, and slightly low results for sample 6. It appears that use of techniques to minimize sodium interference would result in increased accuracy for the potassium determination.

FIGURE 6. TWO-SAMPLE CHARTS & STATISTICS FOR POTASSIUM, FWPCA METHOD

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE	1.5	1.4	8.0	7.5	20.0	19.0
ARITHMETIC MEAN OF REPORTED VALUES, mg/l	1.57	1.49	8.60	8.14	21.5	20.4
RELATIVE ERROR (% BIAS)	+4.76	+6.63	+7.58	+8.66	+7.36	+7.37
STANDARD DEVIATION	0.17	0.22	0.64	0.66	1.11	1.58
95% CONFIDENCE INTERVAL	1.24-1.90	1.06-1.92	7.35-9.85	6.85-9.43	19.3-23.6	17.3-23.5







Alkalinity/Acidity

In this study of alkalinity/acidity measurements by electrometric endpoint shown in Figure 7, moderate precision was achieved. The standard deviation for alkalinity was 1.2 and 5.3 mg/liter as $CaCO_3$ at the 9 and 120 mg/liter levels. At the 20 mg/liter level of acidity, a standard deviation of 1.8 mg/liter was obtained.

In Figure 7, the alkalinity determination shows a positive bias (high results) at the 10 mg/l level and a negative bias at the 100 mg/l level. Although most laboratories report use of Standard Methods as a reference and this manual gives a method modification for low alkalinity (less than 10 mg/l), only four laboratories reported use of the modification.

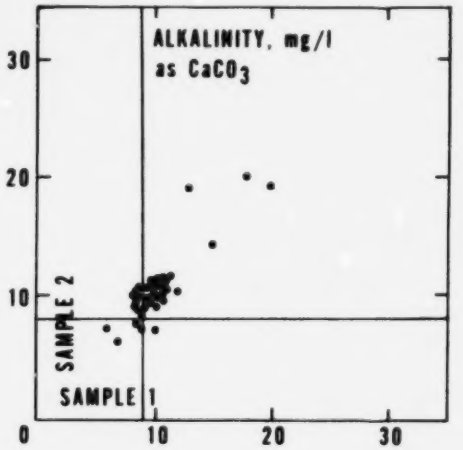
The data for samples 3 and 4 show that most laboratories determined acidity with precision and accuracy well within limits necessary for use in water pollution control. No outliers were rejected for this sample set even though the range of reported results was in excess of 10 mg/l.

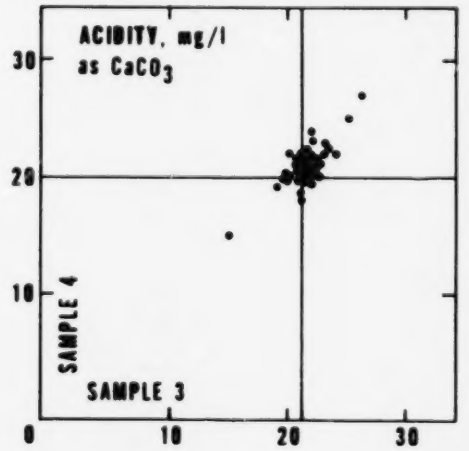
Alkalinity values from three laboratories were rejected as outliers. Two of these showed extremely large positive errors. In the remaining laboratory, one analyst reported very low alkalinity values for samples 1, 2, 5, and 6, while the other analysts' results were acceptable.

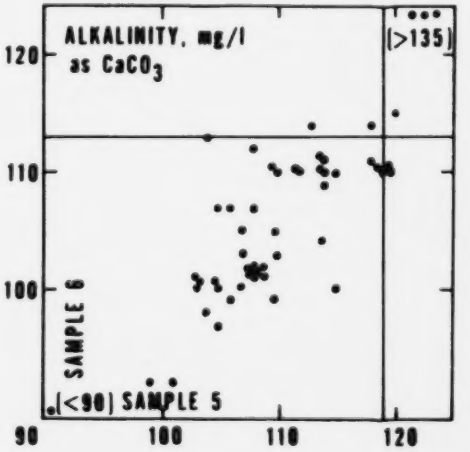
FIGURE 7. TWO-SAMPLE CHARTS & STATISTICS FOR ALKALINITY/ACIDITY, FWPCA METHOD

STATISTIC	SAMPLE					
	1	2	3*	4*	5	6
TRUE VALUE, mg/l as $CaCO_3$	9.0	8.0	21.	20.	119	113
ARITHMETIC MEAN OF REPORTED VALUES, mg/l as $CaCO_3$	9.95	9.78	21.1	20.6	109	105
ACCURACY AS RELATIVE ERROR (% BIAS)	+10.61	+22.29	+0.52	+2.77	-8.19	-7.42
STANDARD DEVIATION, mg/l as $CaCO_3$	1.27	1.14	1.73	1.79	5.28	5.36
95% CONFIDENCE INTERVAL mg/l as $CaCO_3$	7.46-12.4	7.55-12.0	17.7-24.5	17.0-24.1	98.9-120	94.1-115

*ACIDITY







Chloride

The laboratories performed well using the mercuric nitrate volumetric test for chloride at the 100-400 mg/l levels. As seen in Figure 8 the results were very accurate, with almost no bias at these levels. The precision was very good, with a standard deviation ranging from 3 mg/l at the 100 mg/l chloride level to 12 mg/l at the 400 mg/l chloride level. This is similar to the precision reported by Standard Methods, 3.5 mg/l at the 240 mg/l chloride level and somewhat higher than the 2% deviation reported by ASTM.

At the lower chloride levels, 17-18 mg/l of chloride, there was a positive bias of 2-3.5% and a standard deviation of 1.3-1.5 mg/l. Relatively speaking, this was twice the deviation measured at the higher chloride levels.

The *FWPCA Official Interim Methods*, September 1968 lists Standard Methods (12th edition) and ASTM Part 23 as reference sources for chloride. However, the methods are not identical. Standard Methods requires a pH of 2.5 $\pm$ 0.1, while ASTM calls for a pH range of 3.0 to 3.5.

Clark[7] reported the mercuric nitrate method as highly pH dependent; low pH causing high results and high pH causing low results. He produced a curve showing the pH range of 3.0 to 3.5 as the area where minimum error results from slight variation in pH. In the range of pH 2.5, considerably greater error could occur from such small deviations.

Even though both modifications work in their respective pH ranges, it appears that the ASTM procedure offers more precise and reproducible control over pH. The Analytical Method Survey and the subsequent detailed survey on chloride methods indicated:

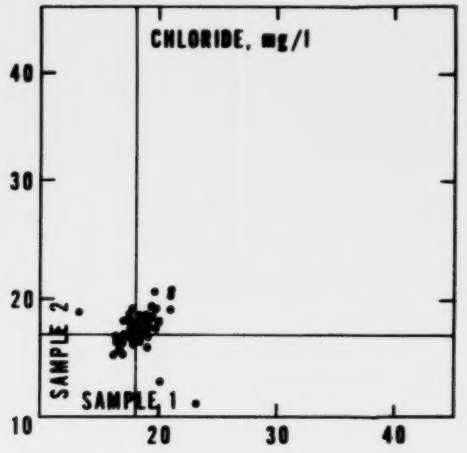
1. There was no correlation between use of fresh vs shelf reagents and the accuracy or precision of data.
2. All FWPCA laboratories except two use the Standard Methods procedure for chloride analysis.
3. Use was reported by two laboratories of each of the following methods: Hach reagents with Standard Methods procedure, Fisher Titralyzer and Autoanalyzer mercuric thiocyanate-method.

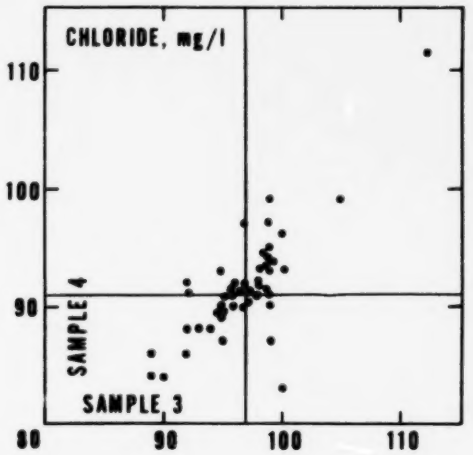
4. There were several comments that the mercuric nitrate method for chlorides was too pH dependent for use and had a poor endpoint.

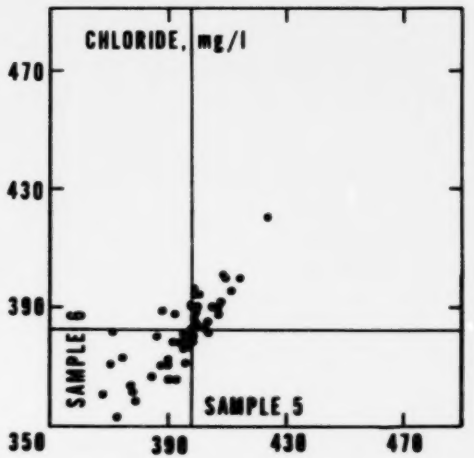
Future tests should be conducted to determine whether the Standard Method and ASTM methods are comparable in precision and accuracy.

FIGURE 8. TWO-SAMPLE CHARTS & STATISTICS FOR CHLORIDE, FWPCA METHOD

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE	18	17	97	91	398	382
ARITHMETIC MEAN OF REPORTED VALUES, mg/l	18.6	17.4	96.5	91.1	393	380
RELATIVE ERROR (% BIAS)	+3.50	+2.16	-0.51	-0.11	-1.19	-0.61
STANDARD DEVIATION	1.32	1.54	3.16	2.92	11.8	11.7
95% CONFIDENCE INTERVAL	16.0 - 21.2	14.3 - 20.4	90.3 - 103	85.4 - 96.8	370 - 416	357 - 403







Sulfate

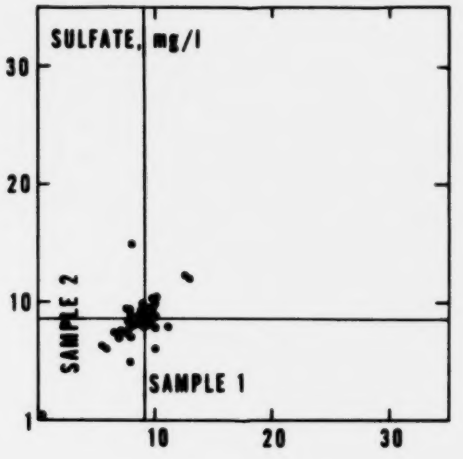
The turbidimetric sulfate determination showed a definite negative bias in this study. Standard Methods estimates the accuracy of the method, under ideal conditions, as ± 10% at concentrations below 10 mg/l, with a rapid decrease in accuracy above 40 mg/l. This study shows improved accuracy as concentrations increased to 200 mg/l. In Figure 9, the spread of values along the 45° line for 3, 4 and 5, 6 suggests a systematic error for the method, caused perhaps by the need to dilute these samples prior to reading.

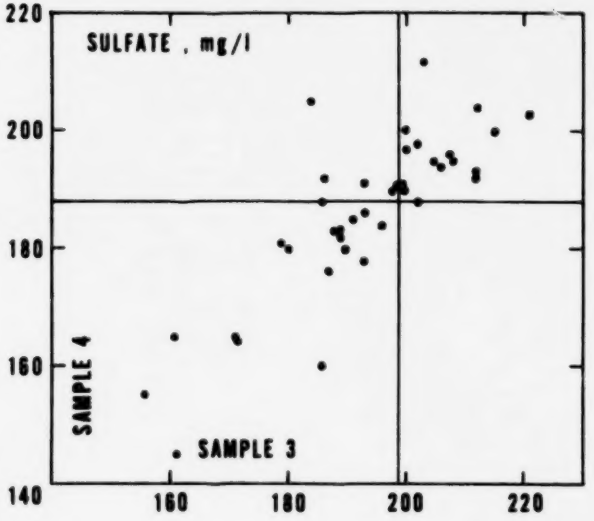
This method is not highly precise. Standard Methods gives standard deviation of ± 28.5 mg/l on a synthetic unknown containing 259 mg/l sulfate. However, *FWPCA Method Study 1* had a standard deviation of only 11.8 mg/l at the 199 mg/l level.

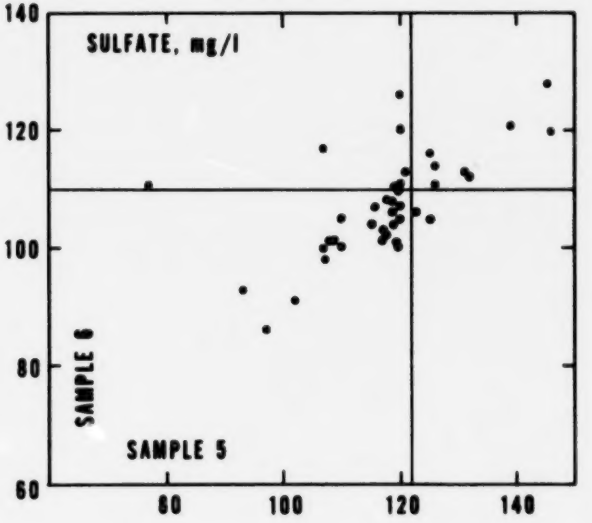
Results from six laboratories were rejected as outliers. All rejected results were low, probably because of inability to obtain a good barium sulfate suspension. Most outliers were found in data for samples 3 and 4, which contained the highest sulfate concentrations. Errors of a magnitude sufficient to be rejected were present less frequently in data for samples 5 and 6, and not at all for samples 1 and 2. Several analysts commented that the turbidimetric method was unsatisfactory because of its slowness and excessive variability with time.

FIGURE 9. TWO-SAMPLE CHARTS & METHOD STATISTICS FOR SULFATE METHOD, FWPCA

STATISTIC	SAMPLE					
	1	2	3	4	5	6
TRUE VALUE, mg/l	9.2	8.6	199	188	122	110
ARITHMETIC MEAN OF REPORTED VALUES, mg/l	8.44	8.28	196	188	118	107
ACCURACY AS RELATIVE ERROR (% BIAS)	-8.26	-3.72	-1.70	+0.04	-3.37	-3.01
STANDARD DEVIATION, mg/l	1.78	2.30	11.8	9.58	7.50	7.86
95% CONFIDENCE INTERVAL, mg/l	4.96-11.9	3.77-12.8	172-219	169-206	103-133	91.3-122







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1. *FWPCA Official Interim Methods for Chemical Analysis of Surface Waters*, September 1968, Federal Water Pollution Control Administration, Analytical Quality Control Laboratory, Cincinnati, Ohio.

2. Youden, W. J. (1967). Statistical Techniques for Collaborative Tests. The Assn. of Official Anal. Chem., Washington, D.C.

3. Analytical Chemistry (1961) 33, 480.

4. Standard Methods for the Examination of Water and Wastewater, 12th ed., 1965.

5. ASTM Standards, Part 23, October 1967.

6. Fishman, Marvin J. The Use of Atomic Absorption for Analysis of Natural Waters. Atomic Absorption Newsletter (Perkin-Elmer Corp.) 5, (5), p.103 (1966).

7. Clark, F. E., Determination of Chloride in Water. Anal. Chem., 22, 553-555 (1950).

Appendices

A. Glossary of Statistical Terms

B. Instrument Survey Listing

APPENDIX A

Glossary of Statistical Terms

Statistical terms used in this evaluation are identical in part with those selected by the Advisory Board of Analytical Chemistry[3].

TRUE-VALUE - The amount of a constituent added, or for an operationally-determined constituent, the average of repeated analyses by the Methods and Performance Evaluation laboratory and at least one referee laboratory.

MEAN - The sum of a series of test results divided by the number in the series. Arithmetic mean is understood.

Precision Data

Measurements of precision relate to the variation among the test results themselves--i.e., the scatter or dispersion of a series of test results, without assumption of any prior information. The following measures apply:

STANDARD DEVIATION - The square root of the variance.

RELATIVE STANDARD DEVIATION - The standard deviation of a series of test results as a percentage of the mean of this series.

95% CONFIDENCE INTERVAL - The interval within which one estimates a given population parameter to lie, 95% of the time.

Accuracy Data

Measurements of accuracy related to the difference between the average test results and the true result when the latter is known or assumed. The following measure applies:

RELATIVE ERROR - The mean error of a series of test results as a percentage of the true result with regard to sign.

APPENDIX B

Instrument Survey

Laboratory	pH Meter	Specific Conductance Meter	Flame Photo-meter	Atomic Absorption Units
R. S. Kerr Water Research Center (Res) Ada, Oklahoma	Beckman Zeromatic	Beckman RC16B2 [II]		P-E 303
Bowser-Morner Testing Labs., Inc. Dayton, Ohio	Photovolt Digicord Beckman Zeromatic	II RC16B2		
Hudson-Delaware Basins Office Edison, N.J.	Beckman Zeromatic	II RC16B2		P-E 303
Alaska Water Lab. College, Alaska	Corning Model 12	Beckman RC16B2 [II]		P-E 303
U.S. Geological Survey Denver, Colorado	Orion Digital Model 801	USGS (1960) WSP-1454, p. 58-60		P-E 303
Cincinnati Water Research Laboratory Cincinnati, Ohio	Beckman Expanded Scale	II RC16B2		P-E 303
Lake Erie Basin Office Cleveland, Ohio	Beckman Zeromatic Model 96	II RC16B2		
Missouri Basin Lab. Kansas City, Missouri	IL Model 205 (Digital)	YSI Model 31		P-E 303
New England Basin Office Needham Heights, Mass.	Fisher Accumet Model 210	II RC16B2		
Southeast Water Lab. Athens, Georgia	Beckman Expando-matic	YSI Model 31		P-E 303
R. S. Kerr Water Research Center (Tech) Ada, Oklahoma	Beckman Zeromatic II	YSI Model 31		
Lower Ohio Basin Office Evansville, Indiana	Beckman Zeromatic	Beckman Portable Model RB-3		P-E 303

APPENDIX B Contd.

Instrument Survey

Laboratory	pH Meter	Specific Conductance Meter	Flame Photo-meter	Atomic Absorption Units
Pacific Northwest Water Laboratory Corvallis, Oregon	Beckman Zeromatic II	II RC16B2		IL 153
National Field Investigations Center	Beckman Zeromatic	II RC18		P-E 303
	IL Model 205	YSI Model 31 II RC16B2		
Lower Mississippi River Basins Comprehensive Project Baton Rouge, La.	IL Delta-matic Model 145	II RB3-338		
Lake Huron Basin Office Grosse Ile, Michigan	Beckman Model K	II RC16B2		
U.S. Geological Survey Austin, Texas	Beckman Zeromatic Model 96	Leeds & Northrup Model 2370-C		P-E 303
Upper Ohio Basin Office Wheeling, West Virginia	IL Model 165	II RC16B2		
National Marine Water Quality Lab. West Kingston, R.I.	Sargent Model DR			P-E 303
Lake Michigan Basin Ofc. Chicago, Illinois	Beckman Zeromatic	II RC16B2	Beckman Model B	
Indiana State Board of Health Indianapolis, Indiana	Beckman Expando-matic	II RC16B1	Beckman DBG with AA attachment but by Flame Emission	
Chesapeake Technical Support Laboratory Annapolis, Maryland	Leeds & Northrup Model 7401			
U.S. Geological Survey Lincoln, Nebraska	Beckman Zeromatic II	Leeds & Northrup	Beckman Model B	
Colorado/Bonneville Basins Laboratory Salt Lake City, Utah	Beckman Zeromatic	II RC16B2	Beckman DU (K+) Technicon Flame Photometer	P-E 303 (Na+)